With 1,2-dichloro or 1,2-dibromoethane, on the other hand, the gold(I) dimer is converted into the Au-Au-bonded gold(II) complex. Ethylene is eliminated in this oxidative-addition process. Compound **2** can also be prepared using chlorine or bromine. Excess halogen will convert either **1** or **2** into the Au(III) complex **3**.

The two-electron reaction between thionyl chloride and the gold(I) dimethylphosphonium bis(methylide) dimer parallels our observed reactions between CoTnPc species and $SOCl_2$. The similarity between these two systems is remarkable; two-electron oxidations are observed with no sign of the one-electron intermediate being formed, and in each case, the one-electron-oxidation product is stable and can be prepared by using alternative methods. The kinetics of the reaction between CoTnPc and $SOCl_2$ are presently being studied to obtain more mechanistic information.[42]

Conclusions

1. Thionyl chloride reacts with $[Co^{I}TnPc(2-)]^-$ and $Co^{II}TnPc(2-)$ to give two-electron-oxidized species (eqs 5 and 6). $[Co^{III}TnPc(2-)]^+$ is oxidized by one electron to $[Co^{III}TnPc(1-)]^{2+}$. $Co^{II}TnPc(2-)$ first forms a mono thionyl chloride adduct and is then oxidized to $Cl_2Co^{III}TnPc(1-)$.

2. A comproportionation reaction is observed between $[Co^{I}TnPc(2-)]^-$ and its two-electron-oxidized product $[Cl_2Co^{III}TnPc(2-)]^-$ (eq 1).

3. The lowest possible oxidation state of CoTnPc in a Li/$SOCl_2$/C battery is $[Co^{I}TnPc(2-)]^-$ due to reduction at the carbon cathode.

4. A two-electron catalytic cycle is indicated for the reduction of thionyl chloride in a Li/$SOCl_2$/(CoTnPc,C) battery. A two-electron-reduction process could result in a safer Li/$SOCl_2$ battery by eliminating reactive intermediates that may form when $SOCl_2$ is reduced by one electron at a carbon cathode not treated with cobalt phthalocyanine.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council (NSERC, Ottawa) and the Office of Naval Research (Washington, DC) for financial support and to the Province of Ontario for a graduate scholarship (P.B.). We are very grateful to S. Greenberg for supplying the CoTnPc and to Dr. Elaine Dodsworth for helpful suggestions in the preparation of the manuscript.

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Lacunar Cyclidene Complexes of Nickel(II) and Cobalt(II) Containing a Misoriented Pendant Base: Synthesis and Characterization of a New T-Form Hemoglobin Model

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A new model for the T-form of hemoglobin has been developed; it consists of a cobalt(II) complex with a pentadentate ligand in which the binding of the axial ligand is inhibited by a steric device. The compounds reported here are isomeric lacunar cyclidene complexes containing a pyridyl group covalently attached to the macrocycle. One isomer possesses a stereochemistry suitable for the intramolecular coordination of the pyridine nitrogen, as demonstrated by ESR experiments on the cobalt(II) complex. The separation of the isomeric components is described together with their characterization. A crystal structure is reported for one of the isomers: (2,3,10,11,13,19-hexamethyl-23-[2-(1-methylpyridiniumyl)]-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4N)nickel(II) iodide, $C_{32}H_5I_3N_7NiH_2O$, orthorhombic, $Pna2_1$, a = 12.247 (2) Å, b = 25.236 (6) Å, c = 12.260 (2) Å, V = 3789 (1) Å^3, Z = 4, and R = 0.056 and R_w = 0.063 for 3534 reflections with $I > 2.5\sigma(I)$. The dioxygen binding ability of the pentadentate isomer of the cobalt(II) complex has been studied, and the observed steric and electronic effects are evaluated as a basis for the control of dioxygen affinity.

Introduction

The study of transition-metal complexes that bind dioxygen reversibly is of interest due to their potential use in dioxygen enrichment/separation and as models for the dioxygen-carrying heme proteins.[2] Complexes derived from pentadentate ligands are particularly attractive since they avoid the need for an exogenous Lewis base. Further, attention to the steric relationships associated with coordination of the appended base can be used to exert unusual control over ligand binding and, thereby, the dioxygen affinity of the complex. Here we report the synthesis and characterization of an unusual pentadentate cyclidene that exhibits impaired dioxygen affinity. This system joins the 2-methyl- and 1,2-dimethylimidazole complexes of various superstructured iron(II) porphyrins[3] as models for the T-form of hemoglobin.[4] In hemoglobin, it is believed that the conformational change associated with cooperative O_2 binding produces the observed reduction in dioxygen affinity by impairment of the axial ligand binding.

Several approaches have been adopted for the incorporation of an additional Lewis base to give a pentadentate ligand, as shown schematically in Figure 1 for complexes of various macrocyclic ligands possessing four other nitrogen donors. Cobalt(II) and iron(II) complexes formed from such pentadentate ligands reversibly bind dioxygen in the absence of added base.[4,5] Very few such complexes have sufficient autoxidation protection of the

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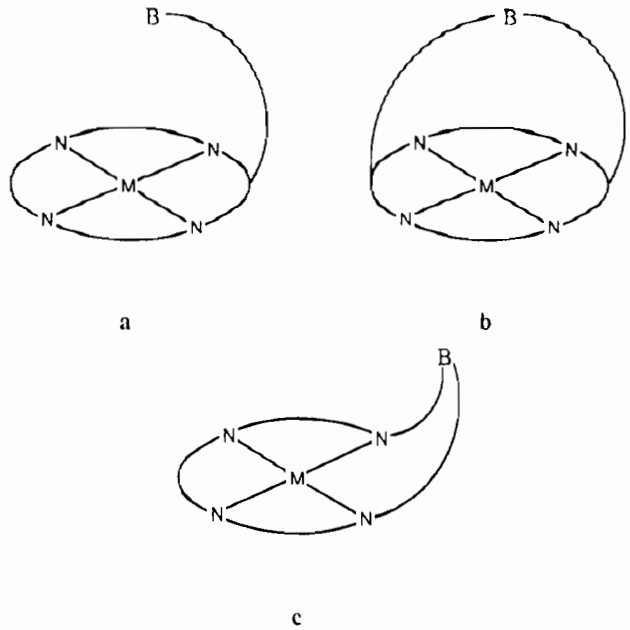
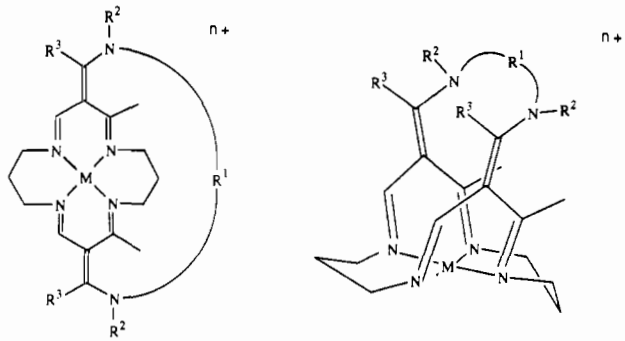


Figure 1. Models for the incorporation of an appended base onto a macrocyclic transition-metal complex.

dioxygen binding site to prevent irreversible oxidation under ambient conditions, although they can be studied at low temperature[6] or by rapid reaction techniques.[7] While these complexes serve to model the role of the protein in natural heme-based systems, they fail to meet the joint requirements of long-term ability to bind dioxygen reversibly, high dioxygen affinity under ambient conditions, and facile control of dioxygen affinity.

Cobalt(II)[2c,8] or iron(II)[8b,9] lacunar cyclidene complexes **1** have been found to bind dioxygen reversibly as dilute solutions in the presence of excess axial base. The stability and affinity of these

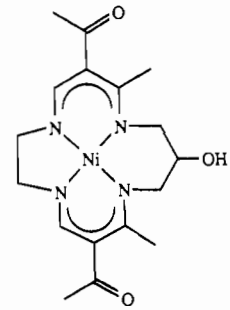


1

complexes can be controlled by structural modifications to the cyclidene ligand, involving a combination of steric and electronic effects. In most general terms, the synthesis, characterization, and study of complexes derived from cyclidene ligands containing a covalently attached base in the vicinity of the metal center is desirable for a number of reasons: it ensures a 1:1 metal:base stoichiometry; it avoids the need for a large excess of base to saturate base-binding equilibria on the unprotected face of tetradentate complex; it avoids multiple equilibria associated with several deoxy species in solution.[9d] Finally, through specific steric relationships, the natural affinity of the cobalt(II) cyclidene complex, having an axial pyridine ligand, can be reduced dramatically by a change that models closely the concept used to explain the reduction in O_2 affinity in hemoglobin when the first oxygens are bound.

This paper describes the synthesis and characterization of nickel(II) lacunar cyclidene complexes containing a pyridyl group attached covalently to the periphery of the macrocycle. These complexes were then converted to the corresponding cobalt(II) complexes, and their reactions with dioxygen were studied.

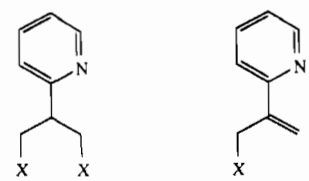
Synthetic considerations led us to examine an approach to a pentadentate cyclidene complexes involving attachment of an axial base as a pendant group (Figure 1a). Examination of crystallographic data for cyclidene complexes led us to conclude that the point of attachment of the arm containing a Lewis base should be a saturated six-membered chelate ring of a tetraaza macrocyclic complex. On the basis of synthetic and symmetry considerations, attachment to the central position was adopted. The preparation of a macrobicyclic complex containing a functional group suitable for attachment of a pendant base in a later step was evaluated but eliminated because of the combination of nucleophilic, electrophilic and basic reagents employed at various stages of the cyclidene synthesis. Structure **2** shows such a macrocyclic nickel(II) complex.[10]



2

Results and Discussion

Synthetic Routes. The introduction of a pendant base into a saturated chelate ring of lacunar cyclidene complexes can be achieved by the use of a 2-substituted 1,3-propanediamine. The precursor, 2-(2-pyridyl)-1,3-propanediol is commercially available, and its transformation into 2-(2-pyridyl)-1,3-propanediamine **3a**



3a	X= NH_2	**4a**	X= NH_2
3b	X= OTs	**4b**	X= OTs
3c	X= Ft	**4c**	X= Ft
3d	X= N_3	**4d**	X= N_3
3e	X= N=PPh_3	**4e**	X= N=PPh_3

has been described.[11] The synthetic procedure reported leads

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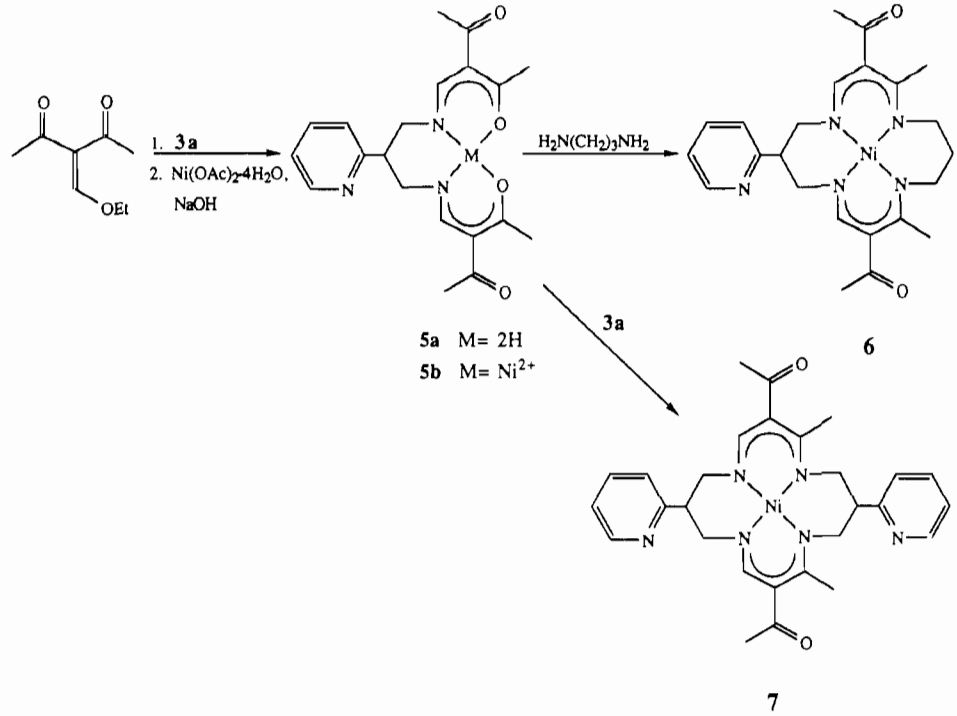
Scheme I



to a mixture of products that was difficult to separate; therefore, efforts were made to find more suitable methods for the transformation. Formation in high yield of a ditosylate **3b** from 2-(2-pyridyl)-1,3-propanediol was achieved by using a literature procedure.[12] Several procedures were attempted for the conversion of the ditosylate **3b** to 2-(2-pyridyl)-1,3-propanediamine **3a**. Attempts to apply the Gabriel synthesis[13] to the ditosylate **3b** gave a white crystalline product that was identified as 2-(2-pyridyl)-3-phthalimido-1-propene (**4c**). Under the conditions employed for the formation of a phthalimide, elimination occurs to generate **4c** presumably via an intermediate **4b**, which then reacts with the phthalimide ion.

The alternative procedure used in these studies for the preparation of **3a** involves the conversion of the ditosylate **3b** to an azide intermediate with sodium azide in dry DMSO, which was then heated at 55 °C for 16 h. The extent of the accompanying elimination reaction was determined with the use of ^{1}H NMR spectroscopy by comparison of (i) the integrals of vinyl protons with those of the pyridyl protons, and (ii) the relative integrals for the singlet at 4.38 ppm, which is assigned to the methylene group in the elimination product **4d**, the doublet centered at 3.65 ppm corresponding to the methylene protons of the diazide **3d**, and the multiplet at 3.30 ppm from the methine proton in the diazide **3d**. The spectra verified the presence of only these two products and showed a typical ratio of components **3d** and **4d** of 4:1 in favor of the diazide. Due to the tendency of azide derivatives to detonate, handling of reaction mixtures was kept to a minimum and samples were used immediately without purification.

Tasker reported a similar procedure for formation of the diazide **3d** using DMF as reaction solvent.[11] While no mention was made of an elimination product for this step, it is likely that this was present, in view of the nature of the byproducts obtained during the reduction step.

Tasker attempted several procedures for the conversion of the diazide **3d** to the corresponding diamine **3a**.[11] The most successful method involved reduction by hydrazine with palladium on carbon as a catalyst, to give a product mixture containing approximately equal amounts of diamine **3a** and the amine of the elimination product **4a**. The elimination product probably resulted in part from contamination of the starting material.

In this work, two reduction methods were examined. For the first, solutions of the azide mixture **3d** and **4d** in ethanol were reduced with hydrogen gas by using 10% palladium on carbon as a catalyst. Although yields were typically 80%, this technique is unsuitable for the generation of large quantities of material because of problems related to reduction of the pyridine nucleus and concomitant production of potent catalyst poisons.[14]

The compounds described here were prepared by using an alternative mild procedure for the conversion of an azide to an amine. This method involves reaction of the azide with a phosphine to give a phosphinimine that can be hydrolyzed under basic conditions.[15] The rapid exothermic reaction of the mixture containing **3d** and **4d** with triphenylphosphine in pyridine occurred quantitatively as judged by the volume of evolved nitrogen. Hydrolysis of the phosphinimine intermediate gave triphenylphosphine oxide and an aqueous solution containing amines **3a** and **4a**. Distillation gave a fraction containing a 4:1 ratio of **3a** to **4a** for use in the following reactions.

General procedures for the formation of macrocyclic precursors to the cyclidene complexes have been developed by Jäger and others.[16,17] A similar route was adopted for the complexes containing a pyridyl group as shown in Scheme I.

Reaction of the distilled diamine/elimination product mixture with 2 equiv of 3-(ethoxymethylidene)-2,4-pentanedione in ethanol at 0 °C gave a creamy white solid that was identified as **5a** on the basis of broad-band-decoupled ^{13}C NMR and infrared spectra. Assuming that 80% of the mass of the amine mixture corresponds to diamine **3a**, the yield for the transformation is in excess of 90%. Metalation of the ligand with sodium hydroxide in ethanol at 50 °C followed by addition of nickel(II) acetate tetrahydrate gave the nickel(II) complex **5b**, which was recrystallized from toluene to give dark red crystals. Identification was based on a combination of ^{13}C and ^{1}H NMR spectroscopy. Alternatively, the reaction sequence from the trihydrochloride salt of **3a** to the nickel(II) N_2O_2 complex **5b** can be carried out in a one-pot procedure in an overall yield of 50%.

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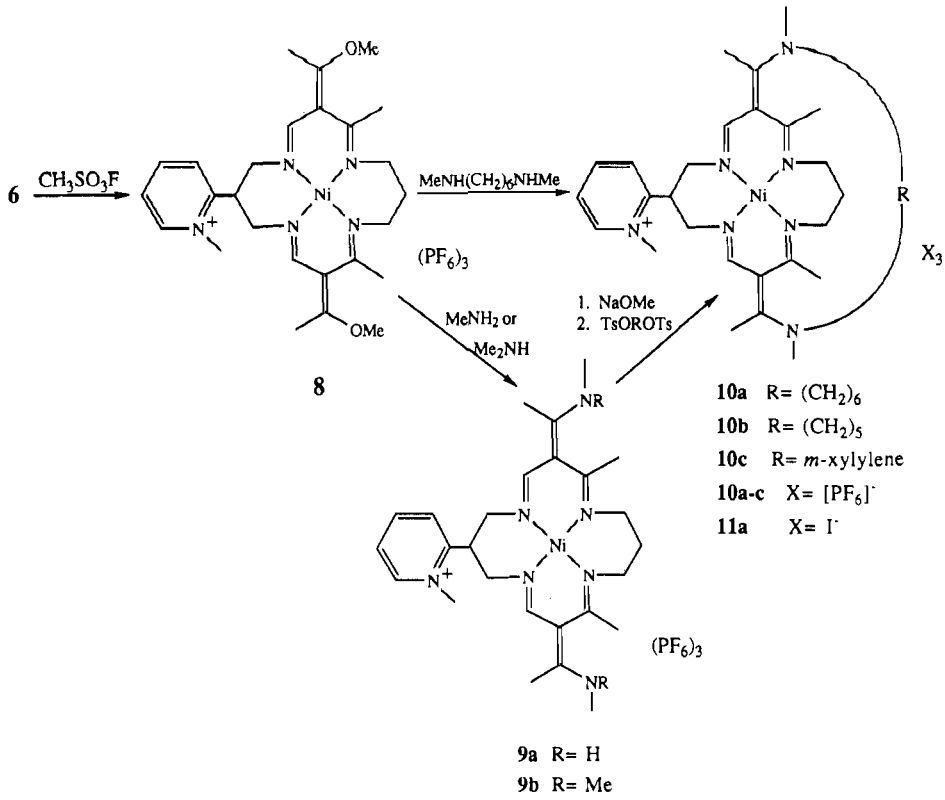
Scheme II



The electrochemical behavior of the neutral nickel(II) complex **5b** was examined by using cyclic voltammetry in DMF containing TBAT. A reversible nickel(III)/nickel(II) couple was observed with $E_{1/2}$ = +0.16 V versus $Ag/AgNO_3$. This compares with a value of +0.32 V under similar conditions for the complex where the pyridyl group is replaced by a hydrogen, suggesting that the pyridyl group is interacting with the metal center.

Macrocyclic ring closure was achieved by using an excess of 1,3-propanediamine. A ^{13}C NMR spectrum of the product showed signals which suggest that the major component corresponds to the macrocyclic complex **6**, although weak signals were observed that correspond to a related complex lacking the pyridyl group. A mass spectrum exhibited molecular ions at 465 and 388 amu that correspond to the parent ions for the pyridyl and non-pyridyl components, respectively. The phenomenon of diamine exchange under the conditions of ring closure has previously been observed.[18] The macrocyclic complex **6** was recrystallized and isolated in pure form and identified on the basis of elemental analysis and infrared and NMR spectroscopy.

Closure of the macrocycle in the nickel(II) pyridyl N_2O_2 complex with the mixture containing the pyridyl diamine **3a** gave **7** (mass spectrum, molecular ion at 542 amu). However, a broad-band-decoupled ^{13}C NMR spectrum showed signals that suggest a mixture of isomers, probably because of the relative orientations of the pyridyl units.

Conversion of the neutral nickel(II) complex to macrobicyclic complexes followed Scheme II. The transformation of the acetyl groups of the coordinated macrocycle **6** to methyl vinyl ether groups (complex **8**) was accomplished by using methyl fluorosulfate in dry dichloromethane. *Caution! Methyl fluorosulfate is an insidious toxin. Fatalities have resulted from inhaling it under conditions that did not seem threatening. Zero personnel exposure is necessary.* Under the conditions employed, methylation also occurs at the pyridyl nitrogen and the tris(hexafluorophosphate) product was isolated, following the addition of ammonium hexafluorophosphate.

Crystallographic studies have shown that nickel(II) complexes containing methyl vinyl ether groups related to **8** are nonplanar and that the vinyl ether groups project on the same side of the mean N_4 plane in the 16-membered ring systems.[19] ^1H and ^{13}C NMR spectra for solutions of **8** show no evidence for the presence of isomeric species despite the presence of the isomeric pyridyl linkage. This indicates that inversion of the saddle conformation of the macrocycle is rapid on an NMR time scale.

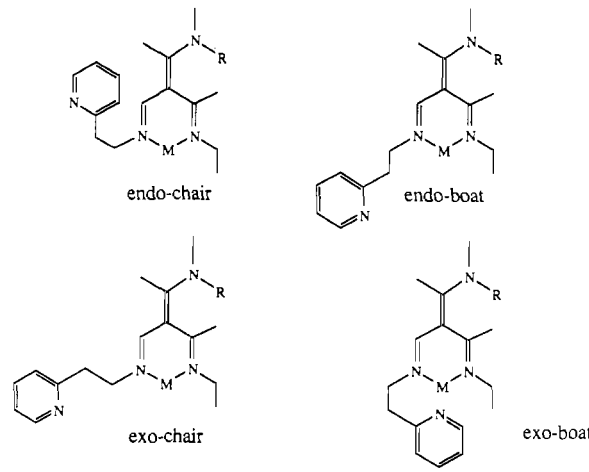


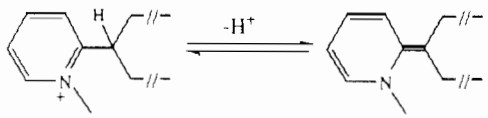
Figure 2. Possible orientations of the appended pyridine base following demethylation.

Substitution of the methoxy groups to give **9a** or **9b** occurs smoothly with methylamine or dimethylamine, respectively. Deprotonation of **9a** with sodium methoxide followed by reaction with alkyl ditosylates leads to the formation of bridged complexes. The bridging step requires high dilution conditions to minimize the formation of oligomeric species. This sequence was used to form products containing a pentamethylene **10b** or a *m*-xylylene **10c** bridge. The nickel(II) complex incorporating a hexamethylene bridge, **10a**, was prepared by the direct high dilution reaction of **8** with *N,N'*-dimethyl-1,6-hexanediamine.

(18) Gustavson, C. R. Ph.D. Thesis, The Ohio State University, 1968.

(19) Alcock, N. W.; Lin, W.-K.; Jircitano, A.; Mokren, J. D.; Corfield, P. W. R.; Johnson, G.; Cairns, C.; Busch, D. H. *Inorg. Chem.* **1987**, *26*, 440.

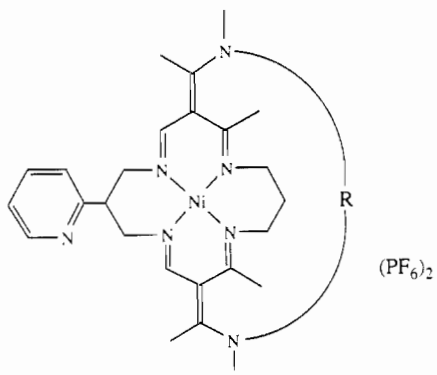
Scheme III



Once bridging has occurred, the orientation of the pyridyl group becomes fixed since the faces of the macrocycle are no longer equivalent, and two isomers are formed, as shown in Figure 2. This figure is a projection in which the N_4 plane of the donor nitrogens is viewed edge-on and the two unsaturated chelate rings are completely eclipsed. These isomeric species are clearly evident from splittings in the ^1H and ^{13}C NMR spectra. In the ^1H NMR spectra, the signals observed near 4.3 ppm, which correspond to the protons on the methyl group of the pyridinium unit, are split, and the relative integrals suggest that the isomers are formed in approximately equal amounts. ^{13}C NMR spectroscopy also confirmed that the isomers of complexes **10a–c** can be separated by fractional crystallization. The structural assignment for one of the isomers with $R_1 = (CH_2)_6$ was established by using single-crystal X-ray diffraction of a triiodide salt, **11a** (vide infra).

It is important to note that in only one of the configurational isomers is the pyridyl group capable of coordination to a metal center, once its *N*-methyl group has been removed. This is illustrated schematically in Figure 2. Although there is a tendency for the saturated chelate ring to adopt a chair conformation, molecular mechanics calculations indicate that the energy difference between the chair and boat forms is small (~1 kcal/mol).[20] Thus, the pyridyl group of the exo form can easily coordinate because of the facile chair–boat interconversion of the chelate ring.

The removal of methyl groups from 1-methylpyridinium compounds has been achieved by using triphenylphosphine.[21] Demethylations of the macrobicyclic nickel(II) complexes **10** to generate **12** were attempted by reaction of the tris(hexafluoro-



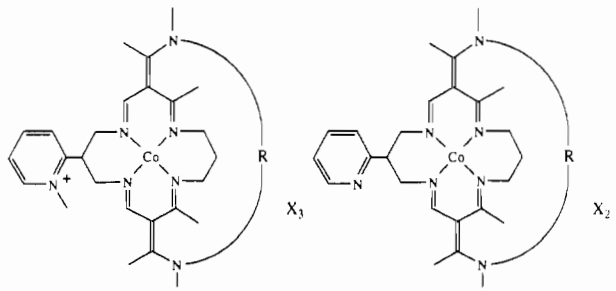
12a R= $(CH_2)_6$
12b R= $(CH_2)_5$
12c R= *m*-xylylene

phosphate) salts with triphenylphosphine in acetonitrile (sealed tube at 150 °C) or DMF (at reflux). The progress of the reaction was monitored by ^1H NMR. Reaction times were 8 days or longer for complete demethylation of the pyridine nitrogen. In contrast, the iodide salts obtained by metathesis underwent smooth demethylation in 5 days or less under the same conditions. These observations are consistent with reports for other 1-methylpyridinium species.[21c]

Applications of the demethylation procedures to isomerically pure starting materials gave mixtures of isomeric products. The isomerism presumably occurs due to the acidity of 2-alkylpyridinium salts as illustrated in Scheme III. Since epimerization during demethylation is unavoidable, no efforts were made to separate isomeric tricationic species prior to demethylation. Unfortunately, attempts to separate the isomers after demethylation using fractional crystallization failed.

It was realized that the cobalt(II) complexes might facilitate isomer separation since only the exo isomer is capable of forming an intramolecular 5-coordinate deoxy complex; this possibility provided an additional motivation for the preparation of that derivative. Of course, the replacement of the nickel(II) ion by iron(II) or cobalt(II) is also necessary to proceed with the study of dioxygen complexes.

In order to form the iron or cobalt complex, the nickel(II) ion must be removed from the macrocycle. Demetalations of cyclidene complexes have been performed by using the procedures outlined in Scheme IV, using hydrogen chloride gas in acetonitrile.[22] The ligands of **10a–c** were isolated as tetrachlorozincate salts and then converted to the corresponding hexafluorophosphate salts **13a–c**.[22] Insertion of cobalt(II) into ligand salts was achieved with the use of cobalt(II) acetate and sodium acetate in methanol,[23] and the corresponding complexes **15a–c** and **16a–c** were isolated. Slow



15a R= $(CH_2)_6$
15b R= $(CH_2)_5$
15c R= *m*-xylylene

16a R= $(CH_2)_6$
16b R= $(CH_2)_5$
16c R= *m*-xylylene

cooling of a methanol solution of the hexamethylene-bridged complex **16a** gave a crystalline material, and concentration of the filtrate gave an orange powder. Elemental analyses indicated that both products correspond to bis(hexafluorophosphate) salts of the cobalt macrocyclic complex **16a**. However, color and solubility differences suggest that the two fractions are stereoisomers. This was supported by spectroscopic investigations, which indicate that the crystalline fraction is the exo isomer.

X-ray Structural Analysis of the Exo Isomer of Complex 11a. The most important result of this analysis is the establishment of the exo conformation for the triiodide salt obtained from the first crystal fraction of the hexamethylene-bridged complex, **11a** (Figure 3). The dimensions are standard for the polymethylene-bridged cyclidenes.[24] It is of interest to note that the $(CH_2)_6$ chain is well-ordered, which is very unusual for chains with an even number of methylene units. This must arise from the unsymmetrical packing of the three iodine atoms, which prevents the complex from lying across a pseudomirror plane. This asymmetry is clearly seen in the packing diagram (Figure 4). The crystal structure presented here provides definitive proof that the synthetic routes used to obtain an appended base have succeeded; the pyridine is in place. Also, since the structural analysis was completed on crystals obtained by fractional crystallization, confident assignment of ^{13}C NMR resonances to isomer type is possible for this particular complex, and by analogy the same assignment is most likely for other compounds of similar structure as well, since all the mixtures exhibit similar spectral patterns.[25]

(20) Schneider, H. J.; Geshwendtner, W.; Weigend, E. F. *J. Am. Chem. Soc.* **1979**, *101*, 7195.
(21) (a) Aumann, D.; Deady, L. W. *J. Chem. Soc., Chem. Commun.* **1973**, *32*. (b) Berg, U.; Gallo, R.; Matzger, J. *J. Org. Chem.* **1976**, *41*, 2621. (c) Deady, L. W.; Korytsky, O. L. *Tetrahedron Lett.* **1979**, *451*.
(22) Busch, D. H.; Olszanski, D. J.; Stevens, J. C.; Schammel, W. P.; Kojima, M.; Herron, N.; Zimmer, L. L.; Holter, K. A.; Mocak, J. *J. Am. Chem. Soc.* **1981**, *103*, 1472.
(23) Stevens, J. C.; Jackson, P. J.; Schammel, W. P.; Christoph, G. G.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3283.
(24) Alcock, N. W.; Lin, W.-K.; Cairns, C.; Pike, G. A.; Busch, D. H. *J. Am. Chem. Soc.* **1989**, *111*, 6630.

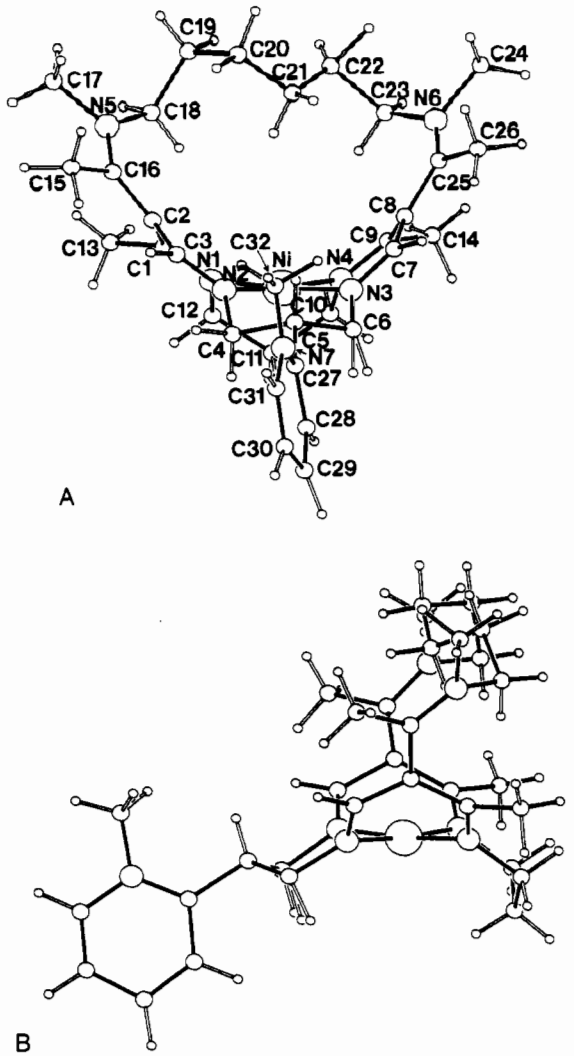


Figure 3. ORTEP drawings of the cation of **11a**, showing atomic numbering.

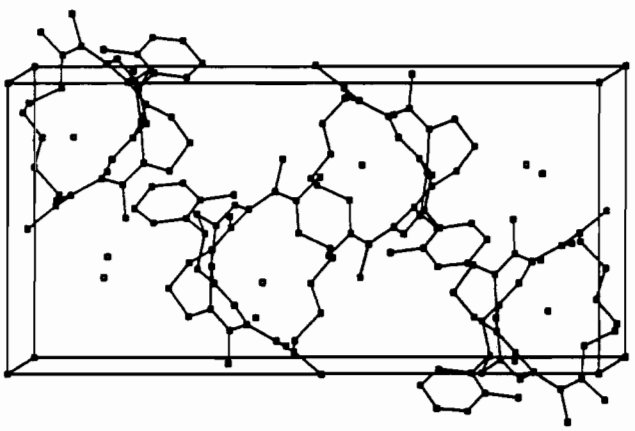


Figure 4. Packing diagram for **11a**, viewed down the *a* axis.

Electron Spin Resonance Spectra. Figure 5 illustrates the ESR spectrum obtained by using the first crystallization fraction of **16a** dissolved in an acetone glass at −196 °C. The triplet due to superhyperfine coupling, which is observed on several of the hyperfine signals, indicates that the nitrogen on the appended pyridine ($I = 1$) is coordinated to the metal center. There is no other source of a nitrogen axial base in this system. This supports the conclusion that the complex is the exo isomer, in which the pyridine nitrogen is available for binding to the cobalt center in an axial position. The possibility of an intermolecular interaction

(25) Tweedy, H. E. Ph.D. Thesis, The Ohio State University, 1981.

Table I: Selected Bond Lengths (Å) and Angles (deg)

Ni–N1	1.90 (1)	N6–C24	1.54 (2)
Ni–N2	1.85 (1)	N6–C25	1.30 (2)
Ni–N3	1.90 (1)	N7–C27	1.34 (2)
Ni–N4	1.90 (1)	N7–C31	1.38 (2)
N1–C1	1.28 (1)	N7–C32	1.45 (2)
N1–C12	1.48 (2)	C1–C2	1.42 (2)
N2–C3	1.30 (2)	C2–C3	1.48 (2)
N2–C4	1.52 (2)	C2–C16	1.40 (2)
N3–C6	1.46 (2)	C4–C5	1.53 (2)
N3–C7	1.30 (1)	C5–C6	1.53 (2)
N4–C9	1.31 (1)	C5–C27	1.54 (2)
N4–C10	1.47 (2)	C7–C8	1.39 (2)
N5–C16	1.33 (2)	C8–C9	1.45 (2)
N5–C17	1.50 (2)	C8–C25	1.48 (1)
N5–C18	1.47 (2)	C10–C11	1.51 (2)
N6–C23	1.48 (2)	C11–C12	1.52 (2)
N2–Ni–N1	87.8 (4)	C3–N2–Ni	123.5 (9)
N3–Ni–N1	175.8 (5)	C4–N2–Ni	120.0 (8)
N4–Ni–N1	92.5 (4)	C4–N2–C3	116.7 (10)
N3–Ni–N2	91.2 (4)	C6–N3–Ni	122.6 (7)
N4–Ni–N2	175.0 (5)	C7–N3–Ni	118.9 (8)
N4–Ni–N3	88.3 (4)	C7–N3–C6	118.1 (9)
C1–N1–Ni	123.4 (8)	C9–N4–Ni	121.8 (7)
C12–N1–Ni	117.1 (7)	C10–N4–Ni	117.8 (7)
C12–N1–C1	119.6 (10)	C10–N4–C9	120.4 (9)

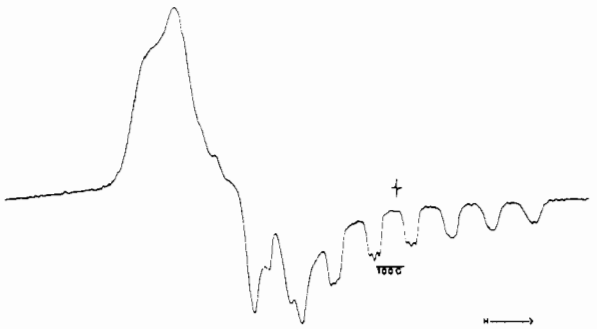


Figure 5. ESR spectrum of *exo*-**16a** in acetone at −196 °C.

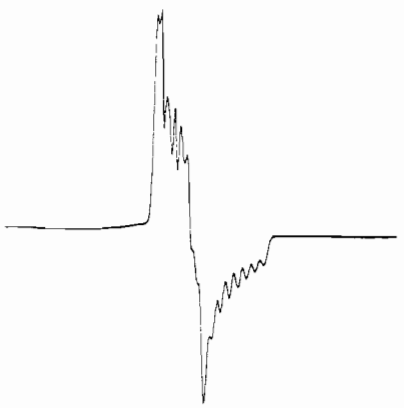


Figure 6. ESR spectrum of the dioxygen adduct of *exo*-**16a** in acetone at −196 °C.

can be excluded because of the extremely dilute sample concentration used (approximately 10^{-4} M) and the steric hindrance to dimerization of the macrocycle structure. When the sample used for obtaining the ESR spectrum shown in Figure 5 was oxygenated at −78 °C, the acetone solution darkened in color. The ESR spectrum obtained from this oxygenated sample is shown in Figure 6. This spectrum is very similar to those of many known dioxygen adducts of cobalt(II) chelates[26] and demonstrates that the formation of the dioxygen adduct is complete at this low temperature. The spectral appearance is attributed to the localization of the electron spin density mainly on the bound dioxygen, effectively

(26) (a) Hoffman, B. M.; Diemente, D. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 61. (b) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295.

Scheme IV

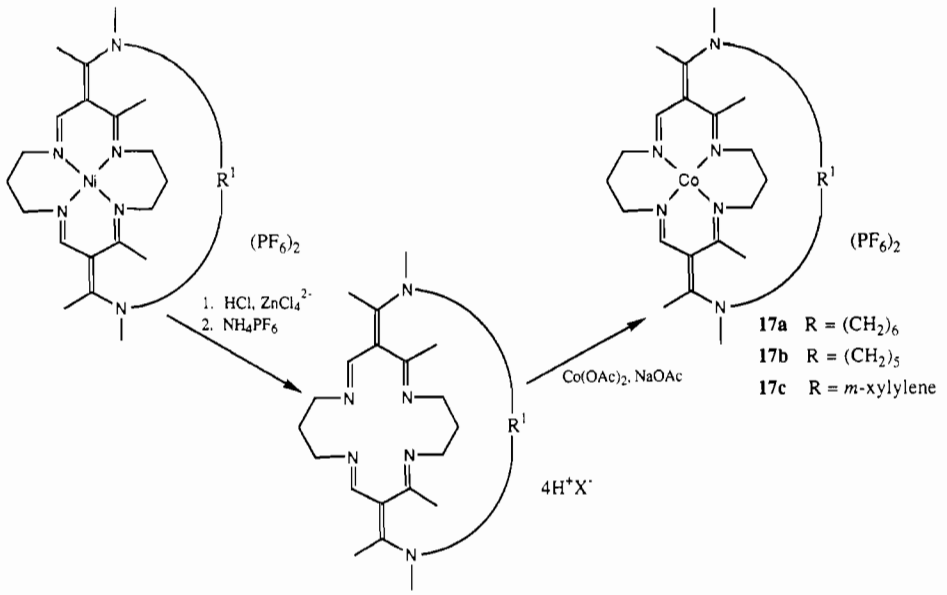


Table II. Atomic Coordinates and Standard Deviations (in Parentheses)

atom	*x*	*y*	*z*
Ni	0.1709 (1)	0.1909 (1)	0.5641 (1)
I1	0.2103 (1)	0.0913 (1)	0.1657 (0)[a]
I2	0.7029 (1)	0.1347 (1)	0.3839 (1)
I3	0.6513 (1)	0.1239 (1)	0.9367 (1)
N1	0.1179 (7)	0.1943 (4)	0.7094 (8)
N2	0.0280 (8)	0.1817 (5)	0.5192 (8)
N3	0.2222 (7)	0.1820 (4)	0.4195 (7)
N4	0.3182 (6)	0.1937 (3)	0.6105 (8)
N5	−0.0469 (8)	0.0533 (4)	0.7896 (8)
N6	0.4630 (8)	0.0497 (4)	0.5412 (9)
N7	−0.0737 (9)	0.1974 (4)	0.1556 (8)
C1	0.0445 (10)	0.1635 (4)	0.7465 (10)
C2	−0.0207 (9)	0.1306 (5)	0.6788 (8)
C3	−0.0402 (10)	0.1506 (5)	0.5678 (11)
C4	−0.0142 (11)	0.2113 (6)	0.4206 (10)
C5	0.0490 (10)	0.1944 (5)	0.3197 (10)
C6	0.1702 (10)	0.2074 (5)	0.3260 (10)
C7	0.2972 (9)	0.1471 (4)	0.4008 (9)
C8	0.3670 (9)	0.1280 (4)	0.4806 (9)
C9	0.3911 (8)	0.1599 (4)	0.5751 (9)
C10	0.3479 (10)	0.2338 (5)	0.6921 (11)
C11	0.2524 (11)	0.2678 (5)	0.7246 (11)
C12	0.1656 (10)	0.2350 (5)	0.7809 (10)
C13	0.0110 (11)	0.1689 (5)	0.8672 (9)
C14	0.5071 (9)	0.1636 (6)	0.6168 (11)
C15	−0.1932 (12)	0.0727 (7)	0.6650 (12)
C16	−0.0807 (10)	0.0867 (5)	0.7128 (11)
C17	−0.1246 (13)	0.0150 (6)	0.8408 (14)
C18	0.0658 (10)	0.0504 (6)	0.8300 (11)
C19	0.1172 (16)	−0.0033 (7)	0.7974 (17)
C20	0.1456 (15)	−0.0100 (7)	0.6803 (17)
C21	0.2309 (15)	0.0241 (7)	0.6363 (13)
C22	0.0349 (15)	0.0092 (8)	0.6839 (15)
C23	0.4293 (11)	0.0520 (5)	0.6564 (11)
C24	0.5398 (12)	0.0027 (6)	0.5178 (14)
C25	0.4229 (8)	0.0772 (4)	0.4620 (10)
C26	0.4354 (11)	0.0569 (5)	0.3504 (11)
C27	−0.0071 (10)	0.2225 (5)	0.2242 (8)
C28	0.0078 (12)	0.2781 (6)	0.2090 (11)
C29	−0.0439 (15)	0.3067 (7)	0.1285 (15)
C30	−0.1221 (13)	0.2764 (5)	0.0669 (13)
C31	−0.1335 (11)	0.2244 (6)	0.0792 (11)
C32	−0.0893 (12)	0.1405 (6)	0.1609 (12)
O1	0.3577 (13)	0.1246 (6)	0.8696 (11)

[a] Fixed coordinate.

producing a cobalt(III) superoxide species.[26b]

Dioxygen Binding. The dioxygen-binding ability of the pentadentate cobalt complex *exo*-**16a** was quantified by using the visible spectrophotometric methods reported by Stevens.[27] The K_{O_2} equilibrium constants at a variety of temperatures are shown in Table III along with the values of the corresponding tetradentate hexamethylene-bridged cobalt cyclidene complex (which does not have an appended axial base) **17a**.[28] Before we proceed, it should be recalled that ESR studies have provided very strong evidence for the coordination of the appended pyridine in these complexes (vide supra).

Table III. Oxygen Binding Data

complex	solvent	axial base	temp, °C	K_{O_2}, Torr^{-1}
17a	CH_3CN	CH_3CN	−34.4	0.062
	CH_3CN	CH_3CN	−27.5	0.043
	CH_3CN	CH_3CN	−20.0	0.026
	CH_3CN	CH_3CN	−10.2	0.006
	CH_3CN	CH_3CN	−4.8	0.005
17a	acetone		−36.3	0.010
	acetone		−30.9	0.006
	acetone		−27.5	0.005
	acetone		−21.0	0.005
17a	acetone	py (1 M)	−20.0	0.68
	acetone	py (1 M)	−10.0	0.19
16a	CH_3CN	py	−38.8	0.022
	CH_3CN	py	−30.4	0.010
	CH_3CN	py	−29.9	0.005
	CH_3CN	py	−19.9	0.004
	CH_3CN	py	−10.0	0.001
16a	acetone	py	−22.2	0.006
	acetone	py	−20.0	0.004
	acetone	py	−19.5	0.004
	acetone	py	−11.8	0.002
	acetone	py	−10.0	0.0014
	acetone	py	−5.0	0.0009
16a	water	py	+2.0	0.003

A remarkable difference in K_{O_2} values is found between the pentadentate ligand derivative having the appended pyridine group **16a**, and the complex without the appended pyridine **17a**. In acetonitrile solution, the dioxygen affinity for the appended pyridine derivative is only about one-sixth that of the corresponding tetradentate complex, where acetonitrile is the axial ligand. This substantial difference is all the more remarkable because axial pyridine is known to promote greater dioxygen affinities than those due to acetonitrile.[9d] If acetonitrile had replaced the appended pyridine as the axial base, it would give K_{O_2} values similar to those seen for complex **17a**. Still more extreme is the difference in O_2

(27) Stevens, J. Ph.D. Thesis, The Ohio State University, 1979.
(28) Stevens, J.; Busch, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 3285.

affinities of these two complexes when they are dissolved in acetone; for the tetradentate case **17a**, the solvent again contains pyridine. The ratio of equilibrium constants is 170–190 in favor of **17a** although the axial base is almost certainly pyridine in both cases. Also, the equilibrium constants for the pentadentate derivative **16a** are essentially independent of solvent for acetone and acetonitrile, a fact that requires coordination of the appended pyridine, since acetone should give a much smaller value of K_{O_2} than acetonitrile. In the face of convincing evidence that the appended pyridine of complex **16a** is coordinated, it must be concluded that the ability of the appended pyridine to promote the dioxygen affinity of the cobalt(II) is substantially impaired as compared to that of free pyridine.

The electrochemistry of **16a** in acetonitrile shows nicely reversible behavior ($E_{3/4-1/4}$ = 60 mV) with an $E_{1/2}$ value of 0.04 V vs Ag/Ag^+ for the Co^{II}/Co^{III} couple. This value is quite negative compared to the value of +0.195 V for the tetradentate complex **17a** under the same conditions.[29] The difference is consistent with the presence of an axial ligand that is stronger than the solvent and is consistent with the binding of the appended pyridine.

Comparison of these electrochemical results and observed K_{O_2} values points out an interesting anomaly. It has been shown for a variety of cobalt dioxygen carriers that a correlation exists between more negative $E_{1/2}$ values and higher K_{O_2} values; this was explained by noting that increasing the electron density at the metal center would result in higher dioxygen binding affinities.[30] This is contradicted by the results obtained for **16a**, where the $E_{1/2}$ value is much more cathodic for the appended base species **16a** than for **17a** but the K_{O_2} value is much lower.

Despite its relatively poor dioxygen binding ability, the appended base complex **16a** is resistant to autoxidation. For example, complete reversibility is observed for *exo*-**16a** at −23 °C when it is exposed to various partial pressures of O_2 and then purged with nitrogen, a process that takes several hours. The corresponding tetradentate complex **17a** shows marked autoxidation under the same conditions. The more negative potential for the Co^{III}/Co^{II} couple of **16a** predicts the converse; the pentadentate derivative should be more easily oxidized.

Clearly from the preceding discussion, the reactions of the new cyclidene complex **16a** with dioxygen are anomalous in more than one sense. We propose that the large reduction in dioxygen affinity arises from the fact that the appended base is restrained by its geometry from optimum coordination to the metal and that the cobalt must lie slightly out of the N_4 coordination plane in order to chelate to the pyridine. It has been argued that in the T-form of hemoglobin,[31] as well as in the model systems of Traylor[32] and Collman,[33] the K_{O_2} values for complexes where the metal is forced out of the coordination plane are lower than when the axial base binding allows the metal to remain in the plane.

The results of X-ray structure determinations show how the appended base in complex **16a** is constrained to a similar behavior. Crystallographic studies[34] on a tetradentate iron(II) cyclidene with an axially bound pyridine show that when a separate pyridine ligand binds to a metal ion, it adopts an orientation in which the pyridine nucleus occupies the groove between the two saturated chelate rings (Figure 7A). In contrast, the appended pyridine ring of complex **16a** (Figure 7B) is constrained to a plane orthogonal to the groove used by the unconstrained pyridine (Figure 7A). The 90° misorientation of the appended pyridine introduces repulsions that could be relieved by displacing the cobalt atom from the coordination plane. In the crystal structures of two iron(II) complexes, the metal atom is displaced about 0.55 Å below the coordination plane, and a very similar structure is anticipated for the deoxy complex of cobalt(II).

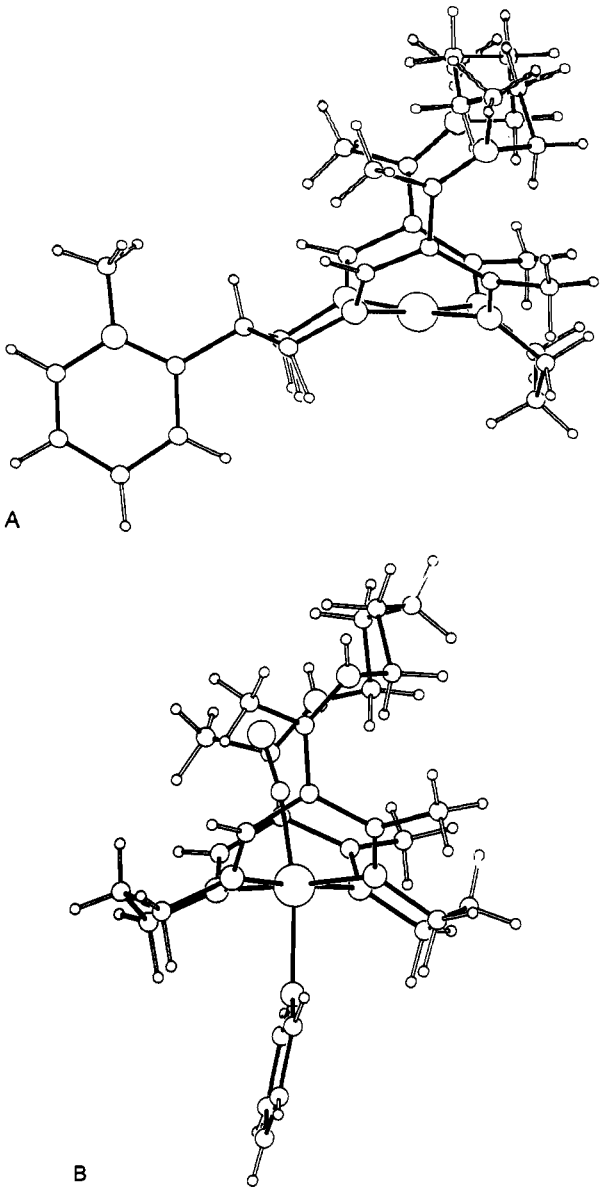


Figure 7. ORTEP drawings illustrating contrasting orientations assumed by appended (A) and free (B) axial base.

The structures of the iron(II) complexes show what happens when a small ligand, such as O_2, binds to the metal atom in a cyclidene complex. As indicated above, in the 5-coordinate species with no ligand in the lacuna, the iron atom occupies a position substantially below the coordination plane. Then, when a small ligand enters the lacuna and binds to the iron (Figure 7A), the iron atom moves up into the coordination plane in order to be within normal bonding distance from the donor atom of the new ligand. Two facts govern what happens when the cobalt(II) appended-pyridine complex **16a** binds to O_2: (1) in the absence of the O_2 the cobalt(II) atom is substantially below the coordination plane; (2) the 90° misorientation of the appended pyridine ligand prevents the cobalt from moving up into that plane in order to bind the dioxygen in the usual manner. The enhanced repulsions associated with this constraint are manifested in a sharp decline in the dioxygen affinity of the complex. This system constitutes a well-defined model for the T-form of hemoglobin.

Experimental Section

General Procedures. All synthesis of organic compounds and compounds containing nickel(II) were routinely conducted under a blanket of nitrogen. Azide-containing organic ligands were at no time heated

(29) Chavan, M. Y.; Meade, T. J.; Busch, D. H.; Kuwana, T. *Inorg. Chem.* **1986**, *25*, 314.
(30) Carter, M. J.; Rilemma, D. P.; Basolo, F. *J. Am. Chem. Soc.* **1974**, *96*, 392.
(31) Perutz, M. F. *Sci. Am.* **1964**, *211*, 64.
(32) Chang, C. K.; Traylor, T. G. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1166.
(33) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Hayes, S. E.; Suslick, K. E. *J. Am. Chem. Soc.* **1978**, *100*, 2761.
(34) Busch, D. H.; Zimmer, L. L.; Grzybowski, J. J.; Olszanski, D. J.; Jackels, S. C.; Callahan, R. C.; Christoph, G. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5919.

above 70 °C, nor were they purified by distillation due to the explosive potential of these compounds.

Catalytic hydrogenations were conducted using a Parr Instrument Co. pressure reaction apparatus equipped with a hydrogen storage tank. Thick-walled pressure-tested bottles were used as reaction vessels.

Reagents. All materials used in this work were reagent grade or better. Solvents were routinely dried over molecular sieves prior to use in reactions performed outside the glovebox. Solvents used in the glovebox were dried by appropriate methods and saturated with nitrogen prior to introduction into the glovebox.

Physical Measurements. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were determined by using a Fisher-Johns melting point apparatus and were uncorrected. Mass spectra were obtained with an MS-9 mass spectrometer and an internal reference of (perfluorotributyl)amine, $(C_4F_9)_3N$ for calibration.

Infrared spectra were obtained on a Perkin-Elmer 283-B infrared spectrometer from 4000 to 250 cm^{-1}. Visible spectra in the region 800–400 nm were measured with a Cary 17D recording spectrophotometer equipped with a variable-temperature cell holder for 1-cm quartz cells. Manipulation of visible spectral data for determination of O_2-binding constants was performed by using the procedure described by Stevens.[28]

^1H nuclear magnetic resonance spectra were recorded with either a Varian 360-L (60-MHz) or a Varian 390-EL (90-MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker WP-80 Fourier transform instrument. Both broad-band-decoupled and off-resonance-decoupling techniques were routinely used for ^{13}C NMR samples. Chemical shifts in ^1H and ^{13}C NMR were assigned relative to a TMS value of 0.0 ppm, usually by direct resonance assignments in the deuterated solvent; in the case of deuterium oxide as solvent, an internal dioxane reference was used.

Electron spin resonance (ESR) spectra were obtained on frozen-glass samples at −196 °C by using a Varian Model 102 ESR spectrometer and quartz sample tubes. The samples were approximately 10^{-4} M in concentration, and tetraalkylammonium salts were added to ensure magnetic dilution and to assist in uniform glass formation. Signal assignments were relative to the signal of a sample with $g = 2.0036$.

Electrochemical analyses were performed on a Princeton Applied Research Corp. Model 173 potentiostat galvanostat equipped with a Model 179 digital coulometer and Model 175 linear programmer. All electrochemical studies were conducted in a Vacuum Atmospheres glovebox containing oxygen-free nitrogen, and current vs potential curves were recorded on a Houston Instruments Model X-Y recorder. The working electrode for voltammograms was a stationary platinum disk, which could be rotated for half-wave potential ($E_{1/2}$) determinations. The solvent used for electrochemical studies was acetonitrile containing tetra-*n*-butylammonium tetrafluoroborate (TBAT) as supporting electrolyte. Values are reported versus an $Ag/AgNO_3$ (0.1 M) standard.

2-(2-Pyridyl)-1,3-bis(*p*-tolylsulfonyl)propane (3b). This compound was prepared according to the method of Tasker and co-workers.[11] Yield: 240 g (78%). Mp: 106 °C (lit.[11] mp 106 °C). ^{13}C NMR: δ 21.6, 45.1, 68.7, 123.6, 124.7, 127.8, 130.8, 132.3, 139.0, 145.2, 147.6, 154.6. ^1H NMR: δ 2.4 (s, 6 H), 3.4 (quin, 1 H), 4.3 (d, 4 H), 6.8–7.7 (m, 11 H), 8.3 (d, 1 H). IR (Nujol): 1600, 1460, 1440, 1360, 1350, 1175 cm^{-1}.

2-(2-Pyridyl)-3-phthalimido-1-propene (4c). DMF (80 mL) containing 2-(2-pyridyl)-1,3-bis(*p*-tolylsulfonyl)propane (20 g, 0.043 mol) was added dropwise to a warmed solution of potassium phthalimide (18.6 g, 0.1 mol) in DMF (100 mL). The mixture was heated at reflux for 4 h, and then approximately half the solvent was removed by distillation under reduced pressure. Addition of water to the residue gave a pale yellow solid that was recrystallized from methanol to give white needle-shaped crystals. Yield: 15 g (84%). Anal. Calcd for $C_{24}H_{17}N_3O_4$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.68; H, 4.79; N, 10.50. Mass spectrum: m/z 264 (M^+). ^{13}C NMR: δ 123.3, 132.2, 134.0, 136.3, 142.0, 148.9, 156.1, 168.0. ^1H NMR: δ 4.9 (s, 2 H), 5.2 (s, 1 H), 5.8 (s, 1 H), 7.0–8.0 (m, 7 H), 8.6 (d, 1 H). IR (Nujol mull): 1715, 1615 cm^{-1}.

2-(2-Pyridyl)-1,3-propanediyl Diazide (3d). Solid sodium azide was added in portions to a solution of 2-(2-pyridyl)-1,3-bis(*p*-tolylsulfonyl)-propane (90 g, 0.195 mol) in dry DMSO (500 mL). The solution was stirred at room temperature for 1 h and then maintained at 55 °C for 16 h. Upon cooling, water (200 mL) was added, and then the solution was extracted with diethyl ether (5 × 75 mL). The ether extracts were combined, washed with water, dried (magnesium sulfate), and then decolorized by stirring with activated charcoal. The solution was filtered and on concentration gave a pale oil in an approximate ratio of 4:1 diazide **3d** to monoazide **4d** based on ^1H NMR integration. The yield corresponds to 85% material recovery. ^{13}C NMR (major product): δ 52.6, 57.2, 113.9, 124.2, 134.7, 141.6. ^1H NMR (product mixture): δ 3.2 (quin, 1 H), 3.6 (d, 4 H), 4.4 (s, 2 H), 5.5 (s, 1 H), 5.9 (s, 1 H), 7.0–7.7 (m, 3 H), 8.5 (d, 1 H). IR (neat): 2100, 1590, 1570, 1470, 1440 cm^{-1}.

2-(2-Pyridyl)-1,3-propanediamine (3a). Procedure i. A solution containing 5.0 g of approximately 80% 2-(2-pyridyl)-1,3-propanediyl diazide in 50 mL of ethanol was mixed with 10% palladium on carbon (0.5 g) in a Parr hydrogenator. The vessel was charged with 45 psi of hydrogen, and then the mixture was shaken at room temperature for 40 h. The reaction could be monitored conveniently by periodic withdrawal of aliquots and observing a decrease in the intensity of the azide stretch at 2100 cm^{-1} in the infrared spectra. The reaction proceded smoothly over a period of 8 h. The catalyst was removed by filtration and the solvent removed to give a golden oil. Once the absence of azide was confirmed by infrared spectroscopy, the oil was purified by vacuum distillation. The distillate was collected over a boiling range from 86 to 110 °C at a pressure of 0.1 mmHg. Yield: 4 g (approximately 80%). ^{13}C NMR: δ 44.2, 53.3, 115.7*, 121.6*, 123.3, 123.8*, 124.9, 138.5*, 148.0*, 149.1*, 149.7, 157.1*, 161.4. ^1H NMR: δ 1.4 (s, 2 H), 2.95 (m, 1 H), 3.0 (d, 4 H), 3.8 (s, 2 H)*, 5.4 (s, 1 H)*, 5.75 (s, 1 H)*, 6.9–7.6 (m, 3 H), 8.5 (d, 1 H). IR (neat): 1595, 1571, 1438, 1478, 1052, 1094 cm^{-1}. In the NMR data an asterisk denotes the resonances corresponding to the major product.

Procedure ii. Crude 2-(2-pyridyl)-1,3-propanediyl diazide (20 g, approximately a 4:1 mixture of **3d**–**4d**) in pyridine (25 mL) was added dropwise over a period of 1 h to a solution of triphenylphosphine (56 g, 1.2 equiv/azide group) in pyridine (100 mL). Evolution of gas was observed, and the mixture was cooled as necessary during the addition and then stirred at room temperature overnight. The solvent was removed by distillation under reduced pressure, and the hot syrupy residue was poured into a 10% ammonium hydroxide solution. The resulting slurry was stirred overnight with an overhead mechanical stirrer. The white precipitate of triphenylphosphine oxide was removed by filtration, and the solid was rinsed with water. The aqueous filtrates were combined and then concentrated to give a pale yellow oil. The oil was examined by infrared spectroscopy to confirm that no azide was present and was purified by vacuum distillation at 0.1 mmHg, collecting the fraction from 104 to 110 °C. Separation of the mixture of **3a** and **4a** was incomplete, but the fraction collected contained a 4:1 ratio of **3a**–**4a** and was suitable for use in the following reactions. Yield: 13.4 g (88%).

2-(2-Pyridyl)-1,3-propanediamine Trihydrochloride. Freshly distilled diamine **3a** (*high boiling fraction*) (2.0 g) was added to diethyl ether saturated with hydrogen chloride. The yellow precipitate obtained in this manner was suspended in a minimum quantity of ethanol and then brought to reflux. A few drops of water were added to obtain a homogeneous solution, and then ethanol saturated in hydrogen chloride was added. Upon cooling, a white crystalline solid was obtained. The solid was collected by filtration, rinsed with diethyl ether, and dried over phosphorus pentoxide. Yield 2.7 g (80%). Anal. Calcd for $C_8H_{16}N_3Cl_3$: C, 36.87; H, 6.19; N, 16.12; Cl, 40.82. Found: C, 36.76; H, 6.28; N, 16.09; Cl, 40.65. ^{13}C NMR: δ 41.6, 41.8, 128.2, 146.0, 147.4, 147.5, 151.2.

3,3′-[(2-(2-Pyridyl)-1,3-propanediyl)bis(iminomethylidyne)]bis[2,4-pentanedione] (5a). Freshly prepared 3-(ethoxymethylidyne)-2,4-pentanedione (48.5 g, 0.31 mol) in ethanol (200 mL) was purged with nitrogen and then cooled to 0 °C. Ethanol (50 mL) containing freshly distilled 2-(2-pyridyl)-1,3-propanediamine/2-(2-pyridyl)prop-2-enylamine (approximately 4:1 molar ratio, 0.13 mol of **3a**) was added over a period of 1 h, and the resulting slurry was stirred at 0 °C for an additional 1 h. The white solid was collected by filtration and then rinsed with diethyl ether. Yield: 43.5 g (90% based on 80% diamine starting material). ^{13}C NMR: δ 26.4, 31.0, 47.9, 51.1, 111.1, 122.5, 124.2, 136.6, 149.5, 156.9, 159.6, 193.7, 199.4. IR (Nujol mull): 3170, 1390, 1030, 995, 975, 930 cm^{-1}.

(3,3′-[(2-(2-Pyridyl)-1,3-propanediyl)bis(iminomethylidyne)]bis[2,4-pentanedionato]-$\kappa^2N\kappa^2O$)nickel(II) (5b). Procedure i. Ethanol (100 mL) containing 3,3′-[(2-(2-pyridyl)-1,3-propanediyl)bis(iminomethylidyne)]-bis[2,4-pentanedione] (**5a**) (8.0 g, 0.0215 mol) and sodium hydroxide (1.72 g, 0.043 mol) was heated at 50 °C to give a homogeneous solution. Addition of nickel(II) acetate tetrahydrate (5.36 g, 0.0215 mol) gave an immediate purple color. After the mixture was heated at reflux for 2 h and cooled to room temperature, a white solid presumed to be sodium acetate was removed by filtration. The solution was placed in a freezer; the lavender solid was collected and recrystallized from toluene to give deep red crystals. Yield: 7.0 g (75%). Anal. Calcd for $C_{20}H_{23}N_3O_4Ni$: C, 56.11; H, 5.42; N, 9.81; Ni, 13.71. Found: C, 56.18; H, 5.51; N, 9.75; Ni, 13.76. IR (KBr pellet): 2920, 1638, 1580 (br), 1290, 995, 935, 620, 545 cm^{-1}.

Procedure ii. A solution containing 2-(2-pyridyl)-1,3-propanediamine trihydrochloride (1.3 g, 0.005 mol) and sodium hydroxide (0.6 g, 0.015 mol) in ethanol (50 mL) was heated at reflux for 1 h. Freshly prepared 3-(ethoxymethylidyne)-2,4-pentanedione was added, and the mixture was

heated at reflux for 30 min. Sequential addition of ethanol (100 mL), sodium hydroxide (0.40 g, 0.01 mol), and nickel(II) acetate tetrahydrate (1.25 g, 0.005 mol) resulted in a purple solution. The solution was heated further at reflux for 2 h, and the product was isolated as described above. Yield: 50% based on 3-(ethoxymethylidyne)-2,4-pentanedione.

(3,11-Diacetyl-2,12-dimethyl-7-(2-pyridyl)-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato-κ^4N)nickel(II) (6). (3,3′-[(2-(2-Pyridyl)-1,3-propanediyl)bis(iminomethylidyne)][bis-2,4-pentanedionato]-$\kappa^2N\kappa^2O$)nickel(II) (5.0 g, 0.0117 mol) was heated at reflux for 20 min in freshly distilled 1,3-propanediamine. Upon cooling, the reaction mixture was poured into cold water and the resulting orange precipitate collected by filtration and rinsed with diethyl ether. A solution of the product in dichloromethane was filtered through Celite to remove traces of metallic nickel. Concentration under reduced pressure gave an orange feathery solid. Yield: 2.3 g (42%). Anal. Calcd for $C_{23}H_{29}N_5O_2Ni$: C, 59.25; H, 6.27; N, 15.02; Ni, 12.59. Found: C, 59.04; H, 6.42; N, 14.95; Ni, 12.42. ^{13}C NMR: δ 19.2, 27.22, 30.2, 47.7, 49.8, 59.6, 116.0, 122.2, 122.4, 136.6, 149.4, 159.0, 160.0, 167.5, 192.2. IR (KBr pellet): 1560 (br), 1500, 1400, 1315, 1010, 955, 750, 542 cm^{-1}.

(3,11-Diacetyl-2,12-dimethyl-7,15-bis(2-pyridyl)-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato-κ^4N)nickel(II) (7). A slurry of 2.5 g (0.0058 mol) of **5b** in 4 mL of the 2-(2-pyridyl)-1,3-propanediamine and 2-(2-pyridyl)prop-2-enylamine mixture gave a deep burgundy-colored solution. The solution was heated for 20 min at 180 °C with the only visual change being the appearance of an orange color. After cooling, the solution was triturated with large amounts of ether, to produce a small amount of orange/pink solid. Yield: 0.5 g (16%). ^{13}C NMR: δ 192.2, 167.8, 159.8, 159.4, 159.2, 158.9, 149.5, 136.7, 122.8, 122.7, 122.2, 116.3, 60.5, 58.9, 54.9, 48.8, 48.5, 47.8, 47.3, 27.1, 19.5, 19.4. ^1H NMR: δ 8.4, 6.8–7.6 (pyridine H's).

(3,11-Bis(1-methoxyethylidene)-2,12-dimethyl-7-[2-(1-methylpyridiniumyl)]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N)nickel(II) Hexafluorophosphate (8). Methyl fluorosulfate (4.3 mL, 0.054 mol) was added to a suspension of (3,11-diacetyl-2,12-dimethyl-7-(2-pyridyl)-1,5,9,13-tetraazacyclohexadeca-1,3,9,11-tetraenato-κ^4N)nickel(II) (**6**) (5 g, 0.0107 mol) in dry dichloromethane (30 mL). The resulting dark homogeneous solution was stirred for 1 h at room temperature, and a lime-colored solid was formed. Methanol (10 mL) was added to consume surplus methylating agent, and the mixture was stirred for 10 min. The solvent was removed under reduced pressure, the solid was dissolved in methanol (100 mL), and methanol containing ammonium hexafluorophosphate (11.0 g, 0.067 mol) was added. The solid was collected by filtration and then recrystallized from an acetonitrile–ethanol mixture to give yellow-green needles. Anal. Calcd for $C_{26}H_{38}N_5O_2P_3F_{18}Ni$: C, 33.00; H, 4.05; N, 7.40; Ni, 6.20. Found: C, 33.20; H, 4.16; N, 7.50; Ni, 6.20. ^{13}C NMR: δ 15.9, 22.3, 28.9, 41.2, 47.3, 51.5, 58.4, 58.7, 117.7, 127.9, 128.1, 147.1, 148.6, 154.5, 166.4, 173.5, 182.3.

(2,12-Dimethyl-3,11-bis[1-(methylamino)ethylidene]-7-[2-(1-methylpyridiniumyl)]-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4N)nickel(II) Hexafluorophosphate (9a). Methylamine gas was passed through a solution of **8** (0.5 g, 0.0005 mol) in acetonitrile (25 mL) for 15 min. The resulting deep red solution was concentrated under reduced pressure, and methanol was added to give a yellow-orange solid. Yield: 0.46 g (94%). Recrystallization was performed by using acetone–water–acetonitrile. Anal. Calcd for $C_{26}H_{40}N_7P_3F_{18}Ni$: C, 33.07; H, 4.27; N, 10.38. Found: C, 33.08; H, 4.31; N, 10.36. ^{13}C NMR: δ 14.8, 20.2, 29.5, 31.5, 42.2, 47.0, 51.0, 58.0, 112.6, 127.3, 127.6, 146.7, 148.0, 155.4, 160.9, 167.8, 170.5. IR (Nujol mull): 3400, 1600, 1580, 1460, 1400, 840, 560 cm^{-1}.

(2,3,10,11,13,19-Hexamethyl-23-[2-(1-methylpyridiniumyl)]-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4N)nickel(II) Hexafluorophosphate (10a). Separate solutions consisting of **8** (1.25 g, 0.0013 mol) in acetonitrile (100 mL) and *N*,*N*′-dimethyl-1,6-hexanediamine (0.19 g, 0.0013 mol) in acetonitrile (100 mL) were added over 3 h to a reservoir of acetonitrile (100 mL) at room temperature with a peristaltic pump. The mixture was stirred for 1 h more, and the solvent was then removed under reduced pressure. The crude material was purified by using chromatography over neutral alumina using acetonitrile as eluant. A broad orange band was collected and then crystallized from acetonitrile–ethanol mixtures. Yield: 1.05 g (78%). Repeated fractional crystallization of the isomers gave pure compounds of each isomer for analysis. Anal. Calcd for $C_{32}H_{50}N_7P_3F_{18}Ni$: C, 37.44; H, 4.91; N, 9.55. Found: C, 37.30 (37.42); H, 4.83 (4.97); N, 9.53 (9.53). ^{13}C NMR (first fraction): δ 20.4, 20.7, 24.1, 25.1, 30.6, 40.1, 40.8, 47.5, 51.5, 57.0, 57.5, 111.2, 127.6, 128.5, 146.6, 148.6, 156.6, 161.2, 167.0, 175.0. ^{13}C NMR (second fraction): δ 20.2, 21.0, 24.4, 25.3, 30.8, 40.8, 43.4, 47.7, 51.6, 57.9, 59.7, 111.4, 127.9, 128.1, 147.5, 148.7, 156.2, 161.7, 167.4, 174.5.

(2,3,9,10,12,18-Hexamethyl-22-[2-(1-methylpyridiniumyl)]-3,9,13,17,20,24-hexaazabicyclo[9.7.7]pentacosa-1,10,12,17,19,24-hexaene-κ^4N)nickel(II) Hexafluorophosphate (10b). Sodium metal (0.20 g, 0.004 mol) was dissolved in methanol (5 mL), and the solution was added to acetonitrile (500 mL) containing **9a** (2.02 g, 0.002 mol). The solution was heated to reflux, and acetonitrile (300 mL) containing 1,5-bis(*p*-tolylsulfonyl)pentane (0.0745 g, 0.0022 mol) was added over 5 h. The mixture was stirred for a further 2 h at reflux; the solution was concentrated to 50 mL under reduced pressure and filtered through Celite. The filtrate was concentrated and subjected to chromatography over neutral alumina using acetonitrile as eluant. A broad orange band was collected and isolated by solvent removal and ethanol addition. Fractional crystallization using acetonitrile–ethanol mixtures gave two isomeric products. Yield: 1.2 g (59%). Anal. Calcd for $C_{31}H_{48}N_7P_3F_{18}Ni$: C, 36.78; H, 4.68; N, 9.69. Found: C, 36.60; H, 5.00; N, 9.64. ^{13}C NMR (first fraction): δ 20.2, 23.5, 26.9, 30.2, 41.3, 43.2, 47.3, 51.1, 57.9, 59.1, 112.1, 127.6, 127.8, 14.7,2 148.3, 160.4, 167.0, 174.7. ^{13}C NMR (second fraction): δ 20.6, 23.7, 27.0, 30.2, 41.7, 51.2, 56.5, 57.9, 59.1, 112.2, 127.7, 128.6, 134.0, 146.3, 147.1, 148.5, 161.5, 175.1.

(2,3,11,12,14,20-Hexamethyl-24-[2-(1-methylpyridiniumyl)]-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9-(28),12,14,19,21,26-nonaene-κ^4N)nickel(II) Hexafluorophosphate (10c). A solution of α,α'-dibromo-*m*-xylene (0.62 g, 0.0023 mol) in acetonitrile (300 mL) and a solution prepared by the addition of sodium metal (0.11 g, 0.004 mol) dissolved in methanol (5 mL) to a solution containing **8** in acetonitrile (295 mL) were added simultaneously over 4 h with a peristaltic pump to a reservoir containing acetonitrile (300 mL) at reflux. After the addition was complete, the mixture was heated at reflux for an additional 1 h. On cooling, the solvent volume was reduced to approximately 50 mL and the precipitate of sodium bromide removed by filtration. The filtrate was purified by chromatography over neutral alumina using acetonitrile as eluant. An orange-yellow band was collected and purified by crystallization from acetonitrile–ethanol to give shiny orange needles. Yield: 1.45 g (60%). Anal. Calcd for $C_{34}H_{46}N_7P_3F_{18}Ni$: C, 39.03; H, 4.43; N, 9.37. Found: C, 39.11; H, 4.59; N, 9.43. ^{13}C NMR (isomer mixture): δ 20.7, 20.9, 30.2, 39.0, 42.8, 45.9, 46.1, 46.9, 47.3, 51.8, 56.9, 59.6, 62.0, 113.4, 113.5, 125.2, 126.6, 126.8, 127.3, 127.5, 127.6, 128.1, 130.4, 130.6, 136.9, 137.9, 146.2, 147.1, 148.2, 148.4, 155.4, 156.0, 156.4, 160.0, 160.4, 166.4, 166.7, 175.8.

(2,3,10,11,13,19-Hexamethyl-23-(2-pyridyl)-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4N)nickel(II) Hexafluorophosphate (12a). Procedure i. Nickel(II) complex **10a** (0.5 g, 0.49 mmol) and triphenylphosphine (0.39 g, 1.5 mmol) in acetonitrile (50 mL) were placed in a sealable tube, and the system was sealed under reduced pressure. The tube was heated at 150 °C for 6–10 days with frequent shaking. Upon cooling, the solvent was removed and the residue purified by chromatography over neutral alumina, eluting with acetonitrile. An orange band was collected, concentrated, and stirred for 30 min at room temperature in an acetone solution containing 4 equiv of tetra-*n*-butylammonium bromide. Following removal of the solvent under reduced pressure, the resulting solid was stirred with water and filtered. The filtrate was introduced onto a Sephadex SP gel column, and the column was washed with distilled water (500 mL). Elution with 0.05 M sodium sulfate gave an initial colorless band, which could be detected by the formation of a cloudy solution with ammonium hexafluorophosphate. A colored band was collected, ammonium hexafluorophosphate was added, and the mixture was concentrated to give a yellow solid. Yield: 50–80%.

Procedure ii. An alternative method was used for reactions on a larger scale. The procedure resembles that described above except that DMF at reflux replaced the use of acetonitrile under sealed conditions. After 6 days, the DMF was removed by distillation, and the residue was stirred with methanol containing ammonium hexafluorophosphate. Chromatography over neutral alumina was followed by purification using Sephadex as described above. Yield: 50–75%. ^{13}C NMR (isomer mixture): δ 19.7, 19.9, 20.6, 24.0, 24.9, 30.2, 30.7, 40.2, 46.2, 48.1, 51.1, 51.3, 57.5, 58.9, 61.0, 110.9, 111.1, 123.2, 123.4, 123.8, 137.7, 138.0, 150.0, 150.2, 160.0, 160.4, 161.0, 167.1, 167.4, 173.4, 173.7.

2,3,10,11,13,19-Hexamethyl-23-(2-pyridyl)-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene Hexafluorophosphate (14a). Hydrogen chloride gas was bubbled through a solution containing the nickel(II) complex **12a** (2.0 g, 0.021 mol) in acetonitrile (50 mL) for 30 min. Zinc metal (2.0 g, 0.031 mol) in acetonitrile was treated with hydrogen chloride gas until a homogeneous solution was obtained. This solution was added dropwise to the solution containing ligand salt to give a white solid. Further solid was obtained by reduction of the solvent volume. The combined solids were washed with ether and then dried under vacuum. Metathesis to hexafluorophosphate salts was performed by the dropwise addition of the tetrachlorozincate salt to an aqueous solution of ammonium hexafluorophosphate. The pale solid was collected by filtration, rinsed with diethyl ether, and dried under reduced pressure. Yield: 50–80%. Ligands prepared in this manner were used without

purification. ^{13}C NMR: δ 19.4, 20.1, 23.6, 24.3, 24.9, 25.4, 26.8, 42.3, 44.8, 50.8, 54.8, 58.2, 125.9, 126.4, 144.2, 146.6, 157.6, 159.0, 180.6.

2,3,10,11,13,19-Hexamethyl-23-[2-(1-methylpyridiniumyl)]-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene hexafluorophosphate (13a), 2,3,9,10,12,18-hexamethyl-22-[2-(1-methylpyridiniumyl)]-3,9,13,17,20,24-hexaazatricyclo[9.7.7]pentacosa-1,10,12,17,20,24-hexaene hexafluorophosphate (13b), and 2,3,11,12,14,20-hexamethyl-24-(2-pyridyl)-3,11,15,19,22,26-hexaazatricyclo[11.7.7.1^{5,9}]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene hexafluorophosphate (13c) were prepared in the manner described for **14a**. **(2,3,10,11,13,19-Hexamethyl-23-[2-(1-methylpyridiniumyl)]-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4*N*)cobalt(II) Hexafluorophosphate (15a).** A solution of **13a** (0.28 g, 0.25 mmol) in methanol (15 mL) was heated at reflux, and a warm solution of sodium acetate (0.034 g, 0.41 mmol) and cobalt(II) acetate (0.125 g, 0.71 mmol) was added. The dark orange solution was heated at reflux for a further 30 min. Upon cooling, a yellow precipitate was obtained that was collected by filtration, rinsed with diethyl ether, and then dried under vacuum. Yield: 0.2 g (78%). Anal. Calcd for $C_{32}H_{50}N_7P_3F_{18}Co$: C, 37.44; H, 4.91; N, 9.55; Co, 5.74; P, 9.05. Found (two determinations): C, 37.40 (37.56); H, 4.86 (5.06); N, 9.68 (9.35); Co, 5.61 (5.61); P, ... (8.99).

(2,3,10,11,13,19-Hexamethyl-23-(2-pyridyl)-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-κ^4*N*)cobalt(II) Hexafluorophosphate (16a). Methanol (15 mL) containing **14a** (0.16 g, 0.14 mmol) was heated at reflux, and methanol (10 mL) containing cobalt(II) acetate (0.05 g, 0.28 mmol) and sodium acetate (0.01 g, 0.14 mmol) was added. The orange solution was heated at reflux for 20 min and allowed to cool to room temperature. A deep red solid was collected by filtration and then dried under vacuum. ESR spectroscopy indicates that this fraction corresponds to the pure exo isomer. Yield: 0.03 g (24%). Further concentration of the solution resulted in the isolation of isomer mixtures containing predominantly the endo isomer. Yield: 0.05 g (45%). Elemental analyses were performed on both fractions. Anal. Calcd for $C_{31}H_{47}N_7P_2F_{12}Co$: C, 42.96; H, 5.46; N, 11.31; P, 7.15; Co, 6.80. Found: C, 42.94 (42.70); H, 5.46 (5.43); N, 11.31 (11.41); P, 7.17 (...); Co, 6.73 (6.89).

Crystal Structure Analysis of Complex 11a. Crystal data: $C_{32}H_5I_3N_7Ni\cdot H_2O$, M_r = 990.2, orthorhombic, $Pna2_1$, a = 12.247 (2) Å, b = 25.236 (6) Å, c = 12.260 (2) Å, V = 3789 (1) Å^3, Z = 4, D_c = 1.74 g cm^{-3}, D_m = 1.61 g cm^{-3}, λ = 0.71069 Å, μ(Mo Kα) = 29.6, T = 20 °C. An isomerically pure sample of compound **10a** was obtained by repeated careful fractional crystallization until purity was confirmed by extended-time FT ^{13}C NMR spectroscopy. The isomerically pure sample was then metathesized to compound **11a**, the iodide salt. Irregular orange-red needles were obtained by slow evaporation of an aqueous solution of **11a**. Data were collected with a Syntex $P2_1$ four circle diffractometer. The maximum 2θ was 50°, with a scan range of ±0.85° (2θ) around the $K\alpha_1$-$K\alpha_2$ angles and scan speed of 2-29° min^{-1}, depending on the intensity of a 2-s prescan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200 reflections and showed a slight decrease during data collection; the data were rescaled to correct for this. Density was measured by flotation. Unit cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections. All 3534 unique reflections ($I/\sigma(I) \geq 2.5$) were used in refinement; they were corrected for Lorentz, polarization, and absorption effects, the last by the analytical method; maximum and minimum transmission factors were 0.68 and 0.54. Crystal dimensions were 0.50 × 1.1 × 0.50 mm.

Systematic absences $0k1$ ($k + l = 2n + 1$) and $h0l$ ($h = 2n + 1$) indicated either the space group $Pna2_1$ or $Pnam$ (nonstandard). Statistical analysis suggested the former, which was shown to be correct by successful refinement. Positions for the three I atoms and one Ni atom were assigned from a Patterson synthesis and the light atoms then found on successive Fourier syntheses (including solvent H_2O). In the final refinement, a weighting scheme

$$w = 1.0/(1 + ((F_o - 60)/25)^2)$$

was used with all hydrogen atom positions (except those on the water molecule) calculated with fixed isotropic temperature factors and all non-hydrogen atoms refined anisotropically. The Z coordinate of I(1) was held fixed to define the origin. The final R values were R = 0.056 and R_w = 0.063. A final difference Fourier map had no electron density areas greater than 0.5 electron in magnitude, indicating that all electron density had been reasonably assigned. Computing was with X-ray 72. Scattering factors and anomalous dispersion factors were taken from ref 35. Final atomic coordinates are given in Table II. Structure factors are given in ref 25.

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Supplementary Material Available: Table S1 (full bond lengths and angles) and Table S2 (anisotropic thermal parameters and H atom coordinates) (5 pages); Table S3 (structure factors) (24 pages). Ordering information is given on any current masthead page.

(35) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

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Axial Ligand Orientation in Iron(II) Porphyrinates. Preparation and Characterization of Low-Spin Bis(imidazole)(tetraphenylporphyrinato)iron(II) Complexes

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The preparation of several low-spin bis(1-substituted imidazole)(tetraphenylporphyrinato)iron(II) complexes is reported (1-substituted imidazole = 1-vinylimidazole, 1-benzylimidazole, 1-methylimidazole, 1-acetylimidazole, and 1-(trimethylsilyl)imidazole). These complexes have been characterized by Mössbauer and UV-vis spectroscopy. The Mössbauer isomer shifts are in the range 0.43-0.47 mm s^{-1} and the quadrupole splittings are in the range 0.97-1.07 mm s^{-1}. The crystal and molecular structure of two of these complexes has been determined by single-crystal X-ray diffraction studies. The two complexes, [Fe(TPP)(1-VinIm)$_2$] and [Fe(TPP)(1-BzlIm)$_2$], have crystallographically imposed inversion centers that lead to parallel ligand plane orientations. Comparisons of the molecular structures of these two species with those of several analogous iron(III) derivatives reveals similar trends in the orientation of the axial imidazole ligands. However, the iron(II) derivatives do show larger axial imidazole "tilts" and "tips". The average Fe-N_p distances are 2.001 (2) Å for [Fe(TPP)(1-VinIm)$_2$] and 1.993 (9) Å for [Fe(TPP)(1-BzlIm)$_2$]; Fe-N(Im) bond distances are 2.004 (2) Å for [Fe(TPP)(1-VinIm)$_2$] and 2.017 (4) Å for [Fe(TPP)(1-BzlIm)$_2$]. Crystal data for [Fe(TPP)(1-VinIm)$_2$]·CH_2Cl_2: monoclinic, $FeCl_2N_8C_{55}H_{42}$, a = 18.871 (4) Å, b = 11.644 (3) Å, c = 22.766 (5) Å, β = 112.90 (1)°, V = 4613.2 Å^3, Z = 4, space group $C2/c$, 4756 observed unique data, all measurements at 293 K. Crystal data for [Fe(TPP)(1-BzlIm)$_2$]: triclinic, $FeN_8C_{64}H_{48}$, a = 10.952 (5) Å, b = 11.402 (5) Å, c = 10.803 (9) Å, α = 104.02 (6)°, β = 105.24 (6)°, γ = 97.65 (4)°, V = 1234.6 Å^3, Z = 1, space group $P\bar{1}$, 3496 observed unique data, all measurements at 118 K.

In hemoproteins, a most interesting physicochemical problem is the wide variation of their physical properties; even those hemoproteins having the same set of heme substituents and the same axial ligands can display remarkably diverse properties.[3] We have

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